

ATTORNEY'S DOCKET NUMBER

U.S. APPLICATION NO. (If known, see 37 CFR 1.5)

INTERNATIONAL FILING DATE

05 September 2000 (5.09.00)

PRIORITY DATE CLAIMED

07 September 1999 (7.09.99)

TITLE OF INVENTION

Recovery of Copper From Copper Bearing Sulphide Minerals by Bioleaching with Controlled Oxygen Feed

APPLICANT(S) FOR DO/EO/US DEW, David William, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). Unexecuted Declaration
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.
14. ☐ A SECOND or SUBSEQUENT preliminary amendment.
15. ☒ A ~~substitute~~ specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

c) International Preliminary Examination Report mailed December 21, 2001

U.S. APPLICATION NO. 37 CFR 1.52		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
P.19496/MAJR		P.19496/MAJR		P.19496/MAJR	
21. <input checked="" type="checkbox"/> The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):					
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO				\$1040.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO				\$890.00	
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO				\$740.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(l)-(4)				\$710.00	
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(l)-(4)				\$100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	890.00
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$	130.00
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	29 - 20 =	9	x \$18.00	\$	162.00
Independent claims	2 - 3 =	0	x \$84.00	\$	0.00
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$280.00	\$	0.00
TOTAL OF ABOVE CALCULATIONS =				\$	1,182.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				\$	0.00
SUBTOTAL =				\$	1,182.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0.00
TOTAL NATIONAL FEE =				\$	1,182.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$	0.00
TOTAL FEES ENCLOSED =				\$	1,182.00
				Amount to be refunded:	\$
				charged:	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$ 1,182.00 to cover the above fees is enclosed.					
b. <input type="checkbox"/> Please charge my Deposit Account No. in the amount of \$ to cover the above fees. A duplicate copy of this sheet is enclosed.					
c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 10-1213 A duplicate copy of this sheet is enclosed.					
d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Jennifer P. Yancy Jones, Tullar & Cooper, P.C. P.O. Box 2266 Eads Station Arlington, VA 22202					
SIGNATURE Jennifer P. Yancy NAME 47,003 REGISTRATION NUMBER					

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:)	
DEW, et al.)	Atty. Docket No. P.19496/MAJR
)	
Application No.: TBA)	
)	
Filed: March 7, 2002)	
)	
For: RECOVERY OF COPPER FROM COPPER)	
BEARING SULPHIDE MINERALS BY)	
BIOLEACHING WITH CONTROLLED)	
OXYGEN FEED)	

PRELIMINARY AMENDMENT

Assistant Commissioner of Patents
Washington, DC 20231

Sir:

This is a Preliminary Amendment in the application filed herewith under 35 U.S.C. 371.

Please amend the above-identified application as follows:

IN THE SPECIFICATIONS:

Please cancel the specification of the subject patent application as filed. That specification corresponds to the specification of PCT/ZA00/00163, filed 5 September 2000, published as WO 01/18269 on 15 March 2001, in favor of the accompanying Substitute Specification. A marked-up copy of the specification, showing the changes made thereto to arrive at the Substitute Specification is enclosed for the Examiner's review.

IN THE CLAIMS:

Please cancel claims 1-47, all of the claims set forth in the specification of the application as filed, without prejudice.

Please add new claims 48-76, as follows:

48. A method of recovering copper from a copper bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C;
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to said slurry;
- (c) controlling dissolved oxygen concentration in said slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: an oxygen content of said feed gas; a feed gas supply rate; a rate of feed of said slurry to said reactor; and
- (d) recovering copper from a bioleach residue of the bioleaching process.

49. The method according to claim 48 further including pre-leaching said slurry prior to said bioleaching process of step (a).

50. The method according to claim 49 wherein said the pre-leaching is effected using an acidic solution of copper and ferric sulphate.

51. The method according to claim 48 further including removing ferric arsenate from said bioleach residue before step (d).

52. The method according to claim 51 further including removing ferric arsenate by precipitation.

53. The method according to claim 48 further including subjecting said bioleach residue to a neutralisation step which produces carbon dioxide which is fed to said feed gas of step (b) or directly to said slurry.

54. The method according to claim 48 further including recovering copper in step (d) using a solvent extraction and electrowinning process.

55. The method according to claim 54 further including feeding oxygen generated during the electrowinning process to said feed gas of step (b), or directly to said slurry.

56. The method according to claim 54 further including supplying raffinate, produced during the solvent extraction, to at least one of the following: said bioleaching process of step (a), and an external heap leach process.

57. The method according to claim 54 further including feeding oxygen generated during said electrowinning process to said feed gas of step (b) or directly to said slurry.

58. The method according to claim 48 wherein said slurry contains at least one of the following: arsenical copper sulphides, and copper bearing sulphide minerals refractory to mesophile leaching.

59. The method according to claim 58 wherein said slurry contain chalcopyrite concentrates.

60. The method according to claim 48 wherein said feed gas contains in excess of 85% oxygen by volume.

61. The method according to claim 48 further including controlling a carbon content of said slurry.

62. The method according to claim 48 further including controlling a carbon dioxide content of said feed gas in a range of from 0.5% to 5.0% by volume.

63. The method according to claim 48 wherein said bioleaching process is carried out at a temperature in a range of from 40°C to 100°C.

64. The method according to claim 63 wherein said temperature is in a range of from 60°C to 85°C.

65. The method according to claim 48 further including bioleaching said slurry at a temperature of up to 45°C using mesophile microorganisms.

66. The method according to claim 65 wherein said microorganisms are selected from the genus groups comprising *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

67. The method according to claim 66 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidithiobacillus thiooxidans*; *Acidithiobacillus ferrooxidans*; *Acidithiobacillus acidophilus*; *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

68. The method according to claim 48 further including bioleaching said slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.

69. The method according to claim 68 wherein said microorganisms are selected from the genus groups comprising *Acidithiobacillus*; *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma*; and *Alicyclobacillus*.

70. The method according to claim 69 wherein said microorganisms are selected from the group comprising *Acidithiobacillus caldus*; *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

71. The method according to claim 64 further including bioleaching said slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

72. The method according to claim 71 wherein said microorganisms are selected from the genus groups comprising *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma*; *Thermoplasma*; and *Picrophilus*.

73. The method according to claim 72 wherein said microorganisms are selected from the group comprising *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

74. A plant for recovering copper from a copper bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a copper bearing sulphide mineral slurry to said vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in a form of oxygen enriched gas or substantially pure oxygen to said slurry, a device which measures a dissolved oxygen concentration in said slurry in said vessel, a control

mechanism whereby, in response to said measured dissolved oxygen concentration, the supply of oxygen from said oxygen source to said slurry is controlled to achieve a dissolved oxygen concentration in said slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers copper from a bioleach residue from said reactor vessel.

75. The plant according to claim 74 wherein said reactor vessel is operated at a temperature in excess of 60°C .

76. The plant according to claim 75 further including a pre-leaching stage for leaching said copper bearing sulphide mineral slurry before said slurry is fed to said reactor vessel.

IN THE ABSTRACT:

Please add the Abstract of the Disclosure as set forth on the separate accompanying sheet.

REMARKS

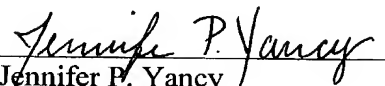
The specification of the subject patent application as filed has been canceled in favor of the accompanying Substitute Specification. The specification corresponds to the specification of PCT/ZA00/00163 filed 5 September 2000. This Substitute Specification generally places the specification in a form more in accordance with the U.S. practice. No new matter is added. A marked-up copy of the specification, which shows the changes made thereto to arrive at the Substitute Specification, is provided for the Examiner's review.

Original claims 1-47 have been canceled in favor of new claims 48-76. These newly presented claims are similar to the claims added to the PCT application and have been written in a form more in accordance with U.S. practice and eliminating multiply dependent claims.

A suitable Abstract of the Disclosure has been added. This is generally similar to the Abstract set forth in the published application WO 01/18269. No new matter is being added.

Entry of this Preliminary Amendment prior to the examination of the application on its merits, and prior to the calculation of the filing fee is respectfully requested.

Respectfully submitted,


Jennifer P. Yancy
Reg. No. 47,003

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March 7, 2002

Attorney Docket No. P.19496/MAJR

ABSTRACT OF THE DISCLOSURE

A method of recovering copper from a copper bearing sulphide mineral which includes the steps of subjecting the slurry to a bioleaching process, supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and recovering copper from a bioleach residue of the bioleaching process.

SUBSTITUTE SPECIFICATION— (Atty. Docket # P.19496/MAJR)**RECOVERY OF COPPER FROM COPPER BEARING SULPHIDE MINERALS****BACKGROUND OF THE INVENTION**

5 **[001]** This invention relates to the recovery of copper from copper bearing sulphide minerals.

[002] Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved. For example carrolite and enargite are relatively slow leaching at temperatures below 50°C, and treatment at or below this temperature would result in poor and sub-economic metal extraction.

10 **[003]** The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

[004] The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase.

20 **[005]** The bioleaching of secondary copper bearing sulphide minerals is similarly problematic and to the applicant's knowledge no commercial copper bioleach plants are in operation.

25 **[006]** More particularly chalcopyrite has long been known to be generally refractory to bioleaching using mesophiles. A major challenge is the leaching of chalcopyrite, on an industrial scale, using thermophilic microorganisms.

SUMMARY OF THE INVENTION

[007] The invention provides a method of recovering copper from a copper bearing sulphide mineral slurry which includes the steps of:

- 5 (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
- (c) recovering copper from a bioleach residue of the bioleaching process.

10 **[008]** The method may include the step of pre-leaching the slurry prior to the bioleaching process of step (a). The pre-leaching may be effected using an acidic solution of copper and ferric sulphate.

[009] The method may include the step of removing ferric arsenate from the bioleach residue before step (c). The ferric arsenate may be removed by precipitation.

15 **[010]** The bioleach residue may be subjected to a neutralisation step which produces carbon dioxide which is fed to the feed gas of step (b), or directly to the slurry.

[011] In step (c) copper may be recovered using a solvent extraction and electrowinning process. Oxygen
20 which is generated during the copper electrowinning may be fed to the feed gas of step (b), or directly to the slurry.

[012] Raffinate, produced by the solvent extraction, may be supplied to at least one of the following: the bioleaching process of step (a), and an external heap leach process.

25 **[013]** Oxygen generated during the electrowinning process may be fed to the feed gas of step (b), or directly to the slurry.

[014] The said slurry may contain at least one of the following: arsenical copper sulphides, and copper bearing sulphide minerals which are refractory to mesophile leaching.

[015] The slurry may contain chalcopyrite concentrates.

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[016] As used herein the expression "oxygen enriched gas" is intended to include a gas, eg. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

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[017] Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume ie. is substantially pure oxygen.

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[018] The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

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[019] Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

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[020] The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

[021] The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

[022] The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

[023] The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.

[024] The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

[025] The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

[026] In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

[027] In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

5 *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*);
Acidithiobacillus ferrooxidans (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and
Acidiphilium cryptum.

10 [028] If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile microorganisms may be used. These may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.

15 [029] Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

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[030] It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using thermophilic microorganisms. These may, for example, be selected from the following genus groups:

Acidothermus; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

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[031] Suitable thermophilic microorganisms may, for example, be selected from the following species:

Sulfolobus metallicus; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

[040] The invention further extends to a method of bioleaching an aqueous slurry containing copper bearing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 40°C and

maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

5 **[041]** The dissolved oxygen concentration may be maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry. The temperature is preferably in the range of from 60°C to 85°C .

10 **[042]** The invention further extends to a plant for recovering copper from a copper bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a copper bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers copper from a bioleach residue from the reactor vessel.

15 **[043]** The oxygen may be supplied in the form of oxygen enriched gas or substantially pure oxygen.

[044] The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C .

20 **[045]** The plant may include a pre-leaching stage for leaching the copper bearing sulphide mineral slurry before the slurry is fed to the reactor vessel. In the pre-leaching stage use may be made of an acidic solution of copper and ferric sulphate.

25 **[046]** Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

[047] As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

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[048] For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

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[049] A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, eg. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry.

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[050] Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

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[051] The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

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[052] The method of invention is of particular benefit to chalcopyrite concentrates, which are more-or-less refractory to leaching at mesophile operating temperatures. The method of the invention therefore opens the door to commercial thermophile leaching of chalcopyrite which to the applicant's knowledge was previously

not possible. The added benefits of a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, while still advantageous, are of less significance in this instance.

5 **[053]** Additionally copper bearing sulphide flotation concentrates frequently contain chalcocite and the method of the invention is of particular benefit, because chalcocite has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, will be particularly beneficial during the bioleaching of copper bearing sulphide concentrates containing chalcocite, even at typical mesophile
10 operating temperatures.

15 **[054]** Copper may be recovered from solution by any appropriate process, for example solvent extraction followed by electrowinning, iron precipitation, or by resin-in-pulp applied to the slurry, followed by electrowinning.

[055] If electrowinning is selected as the production method for copper, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

E PC

DESCRIPTION OF PREFERRED EMBODIMENTS

General Principles

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[060] The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen ie. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

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- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops.

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[061] Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

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[062] The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

25

$$R = M \cdot (C^* - C_L) \quad (1)$$

where:

R = Oxygen demand as mass (kg) per unit volume (m³) per unit time(s) (kg/m³/s),

M = Oxygen mass transfer coefficient in reciprocal seconds (s⁻¹),

C* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m³) (kg/m³), and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

[063] The factor ($C^* - C_L$) is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force ($C^* - C_L$) must be increased.

[064] An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

[065] The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

[066] Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

[067] The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

[068] On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

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[069] As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

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[070] The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C :

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the

point where microorganism growth and mineral oxidation are prevented and below the point at which

microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

20

[071] The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

[072] The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m^3 in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen

utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

[073] It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

[074] Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

[075] In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

[076] Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

- 5 [077] At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

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Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A – typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5

Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

[078] The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

[079] Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

[080] Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

[081] The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

[082] In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

[083] A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

5 [084] An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

10 [085] The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

15 [086] The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

20 [087] The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady
25 supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry 20.

[088] Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

[089] Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry ie. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

[090] Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

[091] Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

[092] It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways eg. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

[093] The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

[094] The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

[095] Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas ie. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

[096] The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

[097] The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

[098] The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

[099] Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen ie. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

[100] The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen

concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

[101] The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

[102] The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$. The results of the experiment are presented in Figure 3.

[103] From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

[104] By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from 11.3 kg/m³/day to 33.7 kg/m³/day. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained

5 **[105]** The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C, according to the temperature correction factor. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C .

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[107] The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, as will be appreciated by those skilled in the art, can be applied to copper bearing sulphide minerals in particular.

[108] Figure 5 of the accompanying drawings is a process flow chart illustrating one form of the method of the invention for recovering copper.

[109] In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen and carbon dioxide sources respectively bear the reference numerals 32 and 34. The copper bearing sulphide slurry is labelled with the numeral 50.

5 [110] The flow sheet in Figure 5 is an example of the invention applied to copper bearing sulphide minerals, arsenical sulphides such as enargite, as well as copper bearing sulphide minerals which are refractory to mesophile leaching, such as chalcopyrite.

10 [111] Copper bearing sulphide concentrate slurry 50 is leached in the plant 10 which contains one or more bioleach reactors, using oxygen enriched gas or substantially pure oxygen 32 as the oxidant. The oxygen concentration in the reactor is controlled in a manner which has been described hereinbefore depending on the type of microorganism used. The plant 10 produces a bioleach residue slurry 100 which contains solubilised copper, and iron predominantly in the ferric state.

15 [112] If the copper bearing sulphide concentrate 50 contains arsenical copper sulphide minerals such as enargite then the bioleach residue 100 will contain solubilised arsenic. In this instance the residue 100 is subjected to a liquid-solid separation step 102 producing solids 104 for disposal and solution 106, which is fed to a pH adjustment step 108 in which the pH of the solution is adjusted by the addition of limestone 110, resulting in partial iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

20 [113] Carbon dioxide 114 produced in the step 108 may be fed to the slurry in the plant 10 by being blended with oxygen from the source 32 or with carbon dioxide from the source 34, or by being injected directly into the slurry in the plant.

25 [114] Slurry 116 produced by the step 108 is returned to the main flow line.

[115] If the ferric iron-to-copper ratio in solution is unfavourable for solvent extraction it may also be desirable to carry out the step 108 directly on the bioleach residue 100.

[116] The residue 100, or the slurry 116, as the case may be, is then subjected to a liquid/solid separation step 118 producing solids 120 for disposal, and a solution 122. The solution in turn is fed to a solvent extraction step 124. Strip liquor 126 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 128 from a copper electrowinning step 130 which produces copper metal cathodes 132. Oxygen gas 134 generated at the anode in the electrowinning process is fed to the source 32 to supplement the supply of oxygen to the plant.

[117] Raffinate 136 from the solvent extraction step 124 is neutralised (138) by the addition of limestone 140 and the resulting slurry 142 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach step 10 or, if appropriate, to an external heap leach 144, to satisfy acid requirements of these process.

[118] Optionally, if there is insufficient carbonate in the slurry 50, carbon dioxide 146 which is generated in the neutralisation step 138 may be fed to the slurry in the plant 10 eg. by being blended with the gas stream from the source 32 or by being added to the carbon dioxide source 34.

[119] Figure 6 illustrates another example of the invention wherein a pre-leaching step is applied to a copper bearing sulphide concentrate. Arsenical copper sulphide such as enargite can also be handled in the manner shown in Figure 6.

[120] The bioleaching plant 10 of Figure 1 again bears the reference numeral 10 in Figure 6 and the oxygen and carbon dioxide sources respectively bear the reference numerals 32 and 34.

[121] Copper bearing sulphide concentrate 150 may be pre-leached in one or more pre-leach reactors 152 using a stream 154 of an acidic solution of copper and ferric sulphate which is produced in a manner described hereinafter.

[122] A slurry 156 produced by the pre-leaching stage 152 is then subjected to a liquid/solid separation step 158 producing residue solids 160 which are fed to the bioleaching plant 10, and a solution 162.

[123] If the concentrate 150 contains arsenical copper sulphide minerals such as enargite then the solution 162 and stream 154 each contain solubilised arsenic. In this instance the solution 162 is fed to a pH adjustment step 164 in which the pH of the solution is raised by the addition of limestone 165 and results in iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

[124] A slurry 166 emerging from the step 164 is then subjected to a liquid/solid separation step 168 producing solids 170 for disposal and a solution 172 which is returned to the main flow line.

[125] If the solution 162 and stream 154 do not contain arsenic then the solution 162 is fed to a solvent extraction step 173, which is described later.

[126] The residue slurry 160, which contains non-reacted copper and other sulphide minerals, is leached in the plant 10 which contains one or more bioleach reactors using oxygen enriched gas or substantially pure oxygen 32, as the oxidant, in the manner which has been described hereinbefore. The oxygen concentration in the reactor is controlled to a suitable value, depending on the type of microorganism used.

[127] The bioleaching process produces a bioleach residue slurry 174 which contains solubilised copper and iron predominantly in the ferric state.

[128] The bioleach residue 174 is subjected to a liquid/solid separation step 176 producing solids 178 for disposal and the solution 154 of solubilised copper and iron which is used in the pre-leaching stage 152.

[129] The solution 162 is fed to the solvent extraction step 173. Strip liquor 190 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 192 from a copper electrowinning step 194 which produces copper metal cathodes 196. Oxygen gas 198 generated at the anode during the electrowinning process is directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32.

[130] Raffinate 200 produced during the stage 173 is neutralised (202) with limestone 204 and the resulting slurry 206 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach plant 10 or, if available, to an external heap leach 208 to satisfy acid requirements of those processes. Carbon dioxide 210 produced in the neutralisation step 202 may be directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32 or by being added to the carbon dioxide from the source 34. Carbon dioxide 212 produced in the step 164 may be similarly handled.

Particular Example

[131] Bioleach pilot plant test work was completed, using a chalcopyrite concentrate assaying 32% copper (75% chalcopyrite), on a $\sim 1.1 \text{ m}^3$ pilot plant consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at a temperature of from 77°C to 80°C using a feed slurry containing 10% solids. The microorganisms used were a mixed *Sulfolobus*-like archaea. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Copper Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Cu Dissolution %	Specific Cu Dissolution Rate $\text{kg/m}^3/\text{h}$	Oxygen Uptake (calculated) $\text{kg/m}^3/\text{h}$	Oxygen Uptake (measured) $\text{kg/m}^3/\text{h}$
2.8	60.5	0.312	0.668	0.638
2.4	55.9	0.336	0.718	0.704

[132] Minimal chalcopyrite leaching, possibly reaching 35% copper dissolution, is found to occur at 40°C using mesophiles.

MARKED-UP COPY OF SPECIFICATION - (Atty. Docket. # 19496/MAJR)

RECOVERY OF COPPER FROM COPPER BEARING SULPHIDE MINERALS

BACKGROUND OF THE INVENTION

- 5 This invention relates to the recovery of copper from copper bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved. For example carrolite and enargite are relatively slow leaching at temperatures below 50°C, and treatment at or below this temperature would result in poor and sub-economic metal extraction.

10 The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase^[1,2].

15 The bioleaching of secondary copper bearing sulphide minerals is similarly problematic and to the applicant's knowledge no commercial copper bioleach plants are in operation.

25 More particularly chalcopyrite has long been known to be generally refractory to bioleaching using mesophiles. A major challenge is the leaching of chalcopyrite, on an industrial scale, using thermophilic microorganisms.

SUMMARY OF THE INVENTION

The invention provides a method of recovering copper from a copper bearing sulphide mineral slurry which includes the steps of:

- 5 (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
- (c) recovering copper from a bioleach residue of the bioleaching process.

The method may include the step of pre-leaching the slurry prior to the bioleaching process of step (a). The
10 pre-leaching may be effected using an acidic solution of copper and ferric sulphate.

The method may include the step of removing ferric arsenate from the bioleach residue before step (c). The ferric arsenate may be removed by precipitation.

15 The bioleach residue may be subjected to a neutralisation step which produces carbon dioxide which is fed to the feed gas of step (b), or directly to the slurry.

In step (c) copper may be recovered using a solvent extraction and electrowinning process. Oxygen which is generated during the copper electrowinning may be fed to the feed gas of step (b), or directly to the slurry.

20

Raffinate, produced by the solvent extraction, may be supplied to at least one of the following: the bioleaching process of step (a), and an external heap leach process.

Oxygen generated during the electrowinning process may be fed to the feed gas of step (b), or directly to the
25 slurry.

The said slurry may contain at least one of the following: arsenical copper sulphides, and copper bearing sulphide minerals which are refractory to mesophile leaching.

The slurry may contain chalcopyrite concentrates.

As used herein the expression "oxygen enriched gas" is intended to include a gas, eg. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The
5 expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume ie. is substantially pure oxygen.

10 The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The
15 upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

20 The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

25 The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

- 5 The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.
- 10 The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase
- 15 in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

- 20 In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

- 25 In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*

acidophilus); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.

If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile
5 microorganisms may be used. These may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.

Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

10 *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.

It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using
15 thermophilic microorganisms. These may, for example, be selected from the following genus groups:

Acidothermus; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

Suitable thermophilic microorganisms may, for example, be selected from the following species:

20 *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.

The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In
25 the latter case vents for off-gas may be provided from the reactor.

According to a different aspect of the invention there is provided a method of recovering copper from a slurry containing copper bearing sulphide minerals which includes the steps of bioleaching the slurry using suitable

microorganisms at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering copper from a bioleach residue.

The bioleaching may be carried out at a temperature in excess of 60°C.

5

The dissolved oxygen concentration may be controlled by controlling the addition of gas which contains in excess of 21% oxygen by volume to the slurry.

Preferably the gas contains in excess of 85% by volume.

10

The bioleach residue may be subjected to a separation step to produce residue solids and solution and the copper may be recovered from the solution in any appropriate way, for example by means of a solvent extraction and electrowinning process.

15

The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a copper bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

The feed gas preferably contains in excess of 85% oxygen by volume.

20

The invention further extends to a method of bioleaching an aqueous slurry containing copper bearing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 40°C and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

25

The dissolved oxygen concentration may be maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry. The temperature is preferably in the range of from 60°C to 85°C.

The invention further extends to a plant for recovering copper from a copper bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a copper bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers copper from a bioleach residue from the reactor vessel.

The oxygen may be supplied in the form of oxygen enriched gas or substantially pure oxygen.

The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C.

The plant may include a pre-leaching stage for leaching the copper bearing sulphide mineral slurry before the slurry is fed to the reactor vessel. In the pre-leaching stage use may be made of an acidic solution of copper and ferric sulphate.

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen

concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

- 5 A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, eg. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry.

- 10 Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

- 15 The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

- 20 The method of invention is of particular benefit to chalcopyrite concentrates, which are more-or-less refractory to leaching at mesophile operating temperatures. The method of the invention therefore opens the door to commercial thermophile leaching of chalcopyrite which to the applicant's knowledge was previously not possible. The added benefits of a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, while still advantageous, are of less significance in this instance.

- 25 Additionally copper bearing sulphide flotation concentrates frequently contain chalcocite and the method of the invention is of particular benefit, because chalcocite has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, will be particularly beneficial during the

bioleaching of copper bearing sulphide concentrates containing chalcocite, even at typical mesophile operating temperatures.

Copper may be recovered from solution by any appropriate process, for example solvent extraction followed
5 by electrowinning, iron precipitation, or by resin-in-pulp applied to the slurry, followed by electrowinning.

If electrowinning is selected as the production method for copper, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

10

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of examples with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

15 Figures 2, 3 and 4 shows various results and parameters obtained from operating a bioreactor in the manner described herein with reference to Figure 1, and

Figures 5 and 6 are process flow charts of copper recovery processes according to different forms of the invention.

20 DESCRIPTION OF PREFERRED EMBODIMENTS

General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits
25 the rate of reaction, requires enrichment of the air with oxygen ie. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense⁽³⁾, and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops⁽⁴⁾

5

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

- 10 The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

15
$$R = M \cdot (C^* - C_L) \quad (1)$$

where:

- R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),
- M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),
- C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
- and
- 20 C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

- The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer
- 25 coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach,

however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles

of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C. *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C.

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C:

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which

microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

- 5 In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.
- 10 Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

15

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has

determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A – typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

5

The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

10 In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

15

An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

20 The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

25 The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry

10 20.

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry ie. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways eg. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas ie. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen ie. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

5

The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 10 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a 15 temperature of 77°C, with *Sulfolobus*-like archaea.

The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 20 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$. The results of the experiment are presented in Figure 3.

25

From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor [proposed by Smith et al ⁽⁵⁾] This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾.

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Examples

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, as will be appreciated by those skilled in the art, can be applied to copper bearing sulphide minerals in particular.

Figure 5 of the accompanying drawings is a process flow chart illustrating one form of the method of the invention for recovering copper.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen and carbon dioxide sources respectively bear the reference numerals 32 and 34. The copper bearing sulphide slurry is labelled with the numeral 50.

The flow sheet in Figure 5 is an example of the invention applied to copper bearing sulphide minerals, arsenical sulphides such as enargite, as well as copper bearing sulphide minerals which are refractory to mesophile leaching, such as chalcopyrite.

Copper bearing sulphide concentrate slurry 50 is leached in the plant 10 which contains one or more bioleach reactors, using oxygen enriched gas or substantially pure oxygen 32 as the oxidant. The oxygen concentration in the reactor is controlled in a manner which has been described hereinbefore depending on the type of microorganism used. The plant 10 produces a bioleach residue slurry 100 which contains solubilised copper, and iron predominantly in the ferric state.

If the copper bearing sulphide concentrate 50 contains arsenical copper sulphide minerals such as enargite then the bioleach residue 100 will contain solubilised arsenic. In this instance the residue 100 is subjected to a liquid-solid separation step 102 producing solids 104 for disposal and solution 106, which is fed to a pH adjustment step 108 in which the pH of the solution is adjusted by the addition of limestone 110, resulting in partial iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

Carbon dioxide 114 produced in the step 108 may be fed to the slurry in the plant 10 by being blended with oxygen from the source 32 or with carbon dioxide from the source 34, or by being injected directly into the slurry in the plant.

- 5 Slurry 116 produced by the step 108 is returned to the main flow line.

If the ferric iron-to-copper ratio in solution is unfavourable for solvent extraction it may also be desirable to carry out the step 108 directly on the bioleach residue 100.

- 10 The residue 100, or the slurry 116, as the case may be, is then subjected to a liquid/solid separation step 118 producing solids 120 for disposal, and a solution 122. The solution in turn is fed to a solvent extraction step 124. Strip liquor 126 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 128 from a copper electrowinning step 130 which produces copper metal cathodes 132. Oxygen gas 134 generated at the anode in the electrowinning process is fed to the source 32 to supplement the
15 supply of oxygen to the plant.

Raffinate 136 from the solvent extraction step 124 is neutralised (138) by the addition of limestone 140 and the resulting slurry 142 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach step 10 or, if appropriate, to an external heap leach 144, to satisfy acid requirements of these process.

20

Optionally, if there is insufficient carbonate in the slurry 50, carbon dioxide 146 which is generated in the neutralisation step 138 may be fed to the slurry in the plant 10 eg. by being blended with the gas stream from the source 32 or by being added to the carbon dioxide source 34.

- 25 Figure 6 illustrates another example of the invention wherein a pre-leaching step is applied to a copper bearing sulphide concentrate. Arsenical copper sulphide such as enargite can also be handled in the manner shown in Figure 6.

Copper bearing sulphide concentrate 150 may be pre-leached in one or more pre-leach reactors 152 using a stream 154 of an acidic solution of copper and ferric sulphate which is produced in a manner described hereinafter.

If the concentrate 150 contains arsenical copper sulphide minerals such as enargite then the solution 162 and stream 154 each contain solubilised arsenic. In this instance the solution 162 is fed to a pH adjustment step 164 in which the pH of the solution is raised by the addition of limestone 165 and results in iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

If the solution 162 and stream 154 do not contain arsenic then the solution 162 is fed to a solvent extraction step 173, which is described later.

The residue slurry 160, which contains non-reacted copper and other sulphide minerals, is leached in the plant 10 which contains one or more bioleach reactors using oxygen enriched gas or substantially pure oxygen 32, as the oxidant, in the manner which has been described hereinbefore. The oxygen concentration in the reactor is controlled to a suitable value, depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 174 which contains solubilised copper and iron predominantly in the ferric state.

The bioleach residue 174 is subjected to a liquid/solid separation step 176 producing solids 178 for disposal and the solution 154 of solubilised copper and iron which is used in the pre-leaching stage 152.

- 5 The solution 162 is fed to the solvent extraction step 173. Strip liquor 190 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 192 from a copper electrowinning step 194 which produces copper metal cathodes 196. Oxygen gas 198 generated at the anode during the electrowinning process is directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32.
- 10 Raffinate 200 produced during the stage 173 is neutralised (202) with limestone 204 and the resulting slurry 206 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach plant 10 or, if available, to an external heap leach 208 to satisfy acid requirements of those processes. Carbon dioxide 210 produced in the neutralisation step 202 may be directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32 or by being added to the carbon dioxide from the source
- 15 34. Carbon dioxide 212 produced in the step 164 may be similarly handled.

Particular Example

- 20 Bioleach pilot plant test work was completed, using a chalcopryrite concentrate assaying 32% copper (75% chalcopryrite), on a $\sim 1.1 \text{ m}^3$ pilot plant consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at a temperature of from 77°C to 80°C using a feed slurry containing 10% solids. The microorganisms used were a mixed *Sulfolobus*-like archaea. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas
- 25 mixtures, are shown in Table 3.

Table 3 : Primary Reactor Copper Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Cu Dissolution %	Specific Cu Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h	Oxygen Uptake (measured) kg/m ³ /h
2.8	60.5	0.312	0.668	0.638
2.4	55.9	0.336	0.718	0.704

Minimal chalcopyrite leaching, possibly reaching 35% copper dissolution, is found to occur at 40°C using mesophiles.

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6/ppts

RECOVERY OF COPPER FROM COPPER BEARING SULPHIDE MINERALSBACKGROUND OF THE INVENTION

5 This invention relates to the recovery of copper from copper bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved. For example carrolite and enargite are relatively slow leaching at temperatures below 50°C, and treatment at or below this temperature would result in poor and sub-economic metal extraction.

15 The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase ^(1,2).

The bioleaching of secondary copper bearing sulphide minerals is similarly problematic and to the applicant's knowledge no commercial copper bioleach plants are in operation.

25 More particularly chalcopyrite has long been known to be generally refractory to bioleaching using mesophiles. A major challenge is the leaching of chalcopyrite, on an industrial scale, using thermophilic microorganisms.

The invention provides a method of recovering copper from a copper bearing sulphide mineral slurry which includes the steps of:

- The said slurry may contain at least one of the following: arsenical copper sulphides, and copper bearing sulphide minerals which are refractory to mesophile leaching.

The slurry may contain chalcopyrite concentrates.

As used herein the expression "oxygen enriched gas" is intended to include a gas, eg. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The
5 expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume ie. is substantially pure oxygen.

10 The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The
15 upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

20

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

25 The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

- 5 The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.
- 10 The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase
- 15 in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

- 20 In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

- 25 In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*

According to a different aspect of the invention there is provided a method of recovering copper from a slurry containing copper bearing sulphide minerals which includes the steps of bioleaching the slurry using suitable

microorganisms at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering copper from a bioleach residue.

The bioleaching may be carried out at a temperature in excess of 60°C.

5

The dissolved oxygen concentration may be controlled by controlling the addition of gas which contains in excess of 21% oxygen by volume to the slurry.

Preferably the gas contains in excess of 85% by volume.

10

The bioleach residue may be subjected to a separation step to produce residue solids and solution and the copper may be recovered from the solution in any appropriate way, for example by means of a solvent extraction and electrowinning process.

15 The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a copper bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

The feed gas preferably contains in excess of 85% oxygen by volume.

20

The invention further extends to a method of bioleaching an aqueous slurry containing copper bearing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 40°C and maintaining the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

25

The dissolved oxygen concentration may be maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry. The temperature is preferably in the range of from 60°C to 85°C.

The invention further extends to a plant for recovering copper from a copper bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a copper bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers copper from a bioleach residue from the reactor vessel.

The oxygen may be supplied in the form of oxygen enriched gas or substantially pure oxygen.

The reactor vessel may be operated at a temperature in excess of 60°C and preferably in the range of 60°C to 85°C.

The plant may include a pre-leaching stage for leaching the copper bearing sulphide mineral slurry before the slurry is fed to the reactor vessel. In the pre-leaching stage use may be made of an acidic solution of copper and ferric sulphate.

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred to make use of suitable measurement probes to sample the actual values of the critical parameters.

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen

concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

- 5 A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, eg. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry.

10

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

15

The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

- 20 The method of invention is of particular benefit to chalcopyrite concentrates, which are more-or-less refractory to leaching at mesophile operating temperatures. The method of the invention therefore opens the door to commercial thermophile leaching of chalcopyrite which to the applicant's knowledge was previously not possible. The added benefits of a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, while still advantageous, are of less significance in this instance.

- 25 Additionally copper bearing sulphide flotation concentrates frequently contain chalcocite and the method of the invention is of particular benefit, because chalcocite has a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, will be particularly beneficial during the

bioleaching of copper bearing sulphide concentrates containing chalcocite, even at typical mesophile operating temperatures.

- Copper may be recovered from solution by any appropriate process, for example solvent extraction followed by electrowinning, iron precipitation, or by resin-in-pulp applied to the slurry, followed by electrowinning.

If electrowinning is selected as the production method for copper, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

10

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of examples with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

- 15 Figures 2, 3 and 4 shows various results and parameters obtained from operating a bioreactor in the manner described herein with reference to Figure 1, and

Figures 5 and 6 are process flow charts of copper recovery processes according to different forms of the invention.

20 DESCRIPTION OF PREFERRED EMBODIMENTS

General Principles

- 25 The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits the rate of reaction, requires enrichment of the air with oxygen ie. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of the oxygen to warrant the additional expense ⁽³⁾; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops ⁽⁴⁾.

5

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

- 10 The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

15
$$R = M \cdot (C^* - C_L) \quad (1)$$

where: R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$);

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
and

20 C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach,

however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen content or concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles

of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C. *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C.

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C:

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which

microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

5 In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

10 Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

15

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has

determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A – typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

Figure 1 of the accompanying drawings shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

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The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

10 In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

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An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

20 The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

25 The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry 20.

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry ie. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways eg. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas ie. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen ie. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

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The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

10

The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

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The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$. The results of the experiment are presented in Figure 3.

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From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor proposed by Smith et al ⁽⁵⁾. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾.

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Examples

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, as will be appreciated by those skilled in the art, can be applied to copper bearing sulphide minerals in particular.

Figure 5 of the accompanying drawings is a process flow chart illustrating one form of the method of the invention for recovering copper.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen and carbon dioxide sources respectively bear the reference numerals 32 and 34. The copper bearing sulphide slurry is labelled with the numeral 50.

The flow sheet in Figure 5 is an example of the invention applied to copper bearing sulphide minerals, arsenical sulphides such as enargite, as well as copper bearing sulphide minerals which are refractory to mesophile leaching, such as chalcopyrite.

Copper bearing sulphide concentrate slurry 50 is leached in the plant 10 which contains one or more bioleach reactors, using oxygen enriched gas or substantially pure oxygen 32 as the oxidant. The oxygen concentration in the reactor is controlled in a manner which has been described hereinbefore depending on the type of microorganism used. The plant 10 produces a bioleach residue slurry 100 which contains solubilised copper, and iron predominantly in the ferric state.

If the copper bearing sulphide concentrate 50 contains arsenical copper sulphide minerals such as enargite then the bioleach residue 100 will contain solubilised arsenic. In this instance the residue 100 is subjected to a liquid-solid separation step 102 producing solids 104 for disposal and solution 106, which is fed to a pH adjustment step 108 in which the pH of the solution is adjusted by the addition of limestone 110, resulting in partial iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

Carbon dioxide 114 produced in the step 108 may be fed to the slurry in the plant 10 by being blended with oxygen from the source 32 or with carbon dioxide from the source 34, or by being injected directly into the slurry in the plant.

- 5 Slurry 116 produced by the step 108 is returned to the main flow line.

If the ferric iron-to-copper ratio in solution is unfavourable for solvent extraction it may also be desirable to carry out the step 108 directly on the bioleach residue 100.

- 10 The residue 100, or the slurry 116, as the case may be, is then subjected to a liquid/solid separation step 118 producing solids 120 for disposal, and a solution 122. The solution in turn is fed to a solvent extraction step 124. Strip liquor 126 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 128 from a copper electrowinning step 130 which produces copper metal cathodes 132. Oxygen gas 134 generated at the anode in the electrowinning process is fed to the source 32 to supplement the
15 supply of oxygen to the plant.

Raffinate 136 from the solvent extraction step 124 is neutralised (138) by the addition of limestone 140 and the resulting slurry 142 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach step 10 or, if appropriate, to an external heap leach 144, to satisfy acid requirements of these process.

- 20 Optionally, if there is insufficient carbonate in the slurry 50, carbon dioxide 146 which is generated in the neutralisation step 138 may be fed to the slurry in the plant 10 eg. by being blended with the gas stream from the source 32 or by being added to the carbon dioxide source 34.

- 25 Figure 6 illustrates another example of the invention wherein a pre-leaching step is applied to a copper bearing sulphide concentrate. Arsenical copper sulphide such as enargite can also be handled in the manner shown in Figure 6.

The bioleaching plant 10 of Figure 1 again bears the reference numeral 10 in Figure 6 and the oxygen and carbon dioxide sources respectively bear the reference numerals 32 and 34.

5 Copper bearing sulphide concentrate 150 may be pre-leached in one or more pre-leach reactors 152 using a stream 154 of an acidic solution of copper and ferric sulphate which is produced in a manner described hereinafter.

A slurry 156 produced by the pre-leaching stage 152 is then subjected to a liquid/solid separation step 158 producing residue solids 160 which are fed to the bioleaching plant 10, and a solution 162.

10 If the concentrate 150 contains arsenical copper sulphide minerals such as enargite then the solution 162 and stream 154 each contain solubilised arsenic. In this instance the solution 162 is fed to a pH adjustment step 164 in which the pH of the solution is raised by the addition of limestone 165 and results in iron removal by precipitation. Arsenic which is present in the slurry is also precipitated.

15 A slurry 166 emerging from the step 164 is then subjected to a liquid/solid separation step 168 producing solids 170 for disposal and a solution 172 which is returned to the main flow line.

20 If the solution 162 and stream 154 do not contain arsenic then the solution 162 is fed to a solvent extraction step 173, which is described later.

The residue slurry 160, which contains non-reacted copper and other sulphide minerals, is leached in the plant 10 which contains one or more bioleach reactors using oxygen enriched gas or substantially pure oxygen 32, as the oxidant, in the manner which has been described hereinbefore. The oxygen concentration
25 in the reactor is controlled to a suitable value, depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 174 which contains solubilised copper and iron predominantly in the ferric state.

The bioleach residue 174 is subjected to a liquid/solid separation step 176 producing solids 178 for disposal and the solution 154 of solubilised copper and iron which is used in the pre-leaching stage 152.

The solution 162 is fed to the solvent extraction step 173. Strip liquor 190 from the solvent extraction step is obtained by stripping the loaded solvent with spent electrolyte 192 from a copper electrowinning step 194 which produces copper metal cathodes 196. Oxygen gas 198 generated at the anode during the electrowinning process is directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32.

Raffinate 200 produced during the stage 173 is neutralised (202) with limestone 204 and the resulting slurry 206 is disposed of. A portion of the raffinate may optionally be recycled to the bioleach plant 10 or, if available, to an external heap leach 208 to satisfy acid requirements of those processes. Carbon dioxide 210 produced in the neutralisation step 202 may be directed to the slurry in the plant 10, for example by being added to the gas stream from the oxygen source 32 or by being added to the carbon dioxide from the source 34. Carbon dioxide 212 produced in the step 164 may be similarly handled.

Particular Example

Bioleach pilot plant test work was completed, using a chalcopyrite concentrate assaying 32% copper (75% chalcopyrite), on a ~1.1 m³ pilot plant consisting of 6 reactors configured as 2 primary reactors in parallel followed by 4 secondary reactors in series. The total primary volume was 470l and the total secondary volume was 630l. All test work was carried out at a temperature of from 77°C to 80°C using a feed slurry containing 10% solids. The microorganisms used were a mixed *Sulfolobus*-like archaea. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Copper Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Cu Dissolution %	Specific Cu Dissolution Rate kg/m ³ /h	Oxygen Uptake (calculated) kg/m ³ /h	Oxygen Uptake (measured) kg/m ³ /h
2.8	60.5	0.312	0.668	0.638
2.4	55.9	0.336	0.718	0.704

Minimal chalcopyrite leaching, possibly reaching 35% copper dissolution, is found to occur at 40°C using mesophiles.

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CLAIMS

1. A method of recovering copper from a copper bearing sulphide mineral slurry which includes the steps of:
 - (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C ;
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry;
 - (c) controlling the dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas; the feed gas supply rate; the rate of feed of the slurry to the reactor; and
 - (d) recovering copper from a bioleach residue of the bioleaching process.
2. A method according to claim 1 which includes the step of pre-leaching the slurry prior to the bioleaching process of step (a).
3. A method according to claim 2 wherein the pre-leaching is effected using an acidic solution of copper and ferric sulphate.
4. A method according to any one of claims 1 to 3 which includes the step of removing ferric arsenate from the bioleach residue before step (d).
5. A method according to claim 4 wherein the ferric arsenate is removed by precipitation.
6. A method according to any one of claims 1 to 5 wherein the bioleach residue is subjected to a neutralisation step which produces carbon dioxide which is fed to the feed gas of step (b) or directly to the slurry.
7. A method according to any one of claims 1 to 6 wherein in step (d) copper is recovered using a solvent extraction and electrowinning process.

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8. A method according to claim 7 wherein oxygen generated during the copper electrowinning is fed to the feed gas of step (b), or directly to the slurry.
9. A method according to claim 7 or 8 wherein raffinate, produced during the solvent extraction, is supplied to at least one of the following: the bioleaching process of step (a), and an external heap leach process.
10. A method according to any one of claims 7 to 9 wherein oxygen generated during the electrowinning process is fed to the feed gas of step (b) or directly to the slurry.
11. A method according to any one of claims 1 to 10 wherein the said slurry contains at least one of the following: arsenical copper sulphides, and copper bearing sulphide minerals refractory to mesophile leaching.
12. A method according to claim 11 wherein the said slurry contain chalcopyrite concentrates.
13. A method according to any one of claims 1 to 12 wherein the feed gas contains in excess of 85% oxygen by volume.
14. A method according to any one of claims 1 to 13 which includes the step of controlling the carbon content of the slurry.
15. A method according to any one of claims 1 to 14 which includes the step of controlling the carbon dioxide content of the feed gas in the range of from 0.5% to 5.0% by volume.
16. A method according to any one of claims 1 to 15 wherein the bioleaching is carried out at a temperature in the range of from 40°C to 100°C.
17. A method according to claim 16 wherein the said temperature is in the range of from 60°C to 85°C.

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18. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.
19. A method according to claim 18 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptospirillum*; *Ferromicrobium*; and *Acidiphilium*.
20. A method according to claim 18 or 19 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.
21. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.
22. A method according to claim 21 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.
23. A method according to claim 21 or 22 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.
24. A method according to claim 17 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.
25. A method according to claim 24 wherein the microorganisms are selected from the following genus groups: *Acidotherrmus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.

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26. A method according to claim 24 or 25 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.
27. A plant for recovering copper from a copper bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a copper bearing sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched gas or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers copper from a bioleach residue from the reactor vessel.
28. A plant according to claim 27 wherein the reactor vessel is operated at a temperature in excess of 60°C.
29. A plant according to claim 27 or 28 which includes a pre-leaching stage for leaching the copper bearing sulphide mineral slurry before the slurry is fed to the reactor vessel.

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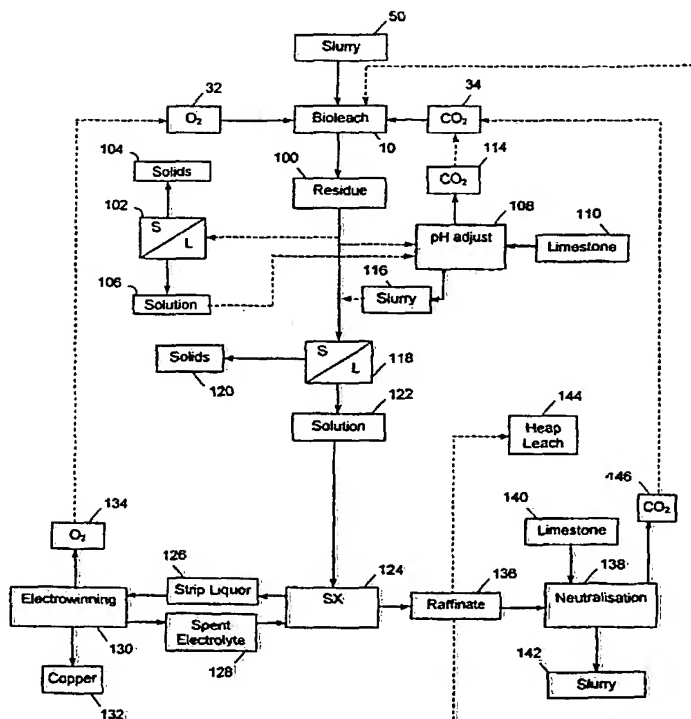
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99/5746 7 September 1999 (07.09.1999) ZA</p> <p>(71) Applicant (for all designated States except US): BILLITON INTELLECTUAL PROPERTY B.V. [NL/NL]; Mariahoeveplein 6, NL-2509 AA The Hague (NL).</p> | <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): DEW, David, William [ZA/ZA]; 33 Alphen Close, Wroxham Road, Paulshof, 2196 Sandton (ZA). BASSON, Petrus [ZA/ZA]; 10 Lourie's Loft, Perm Street, Sonneglans, 2194 Randburg (ZA). MILLER, Deborah, Maxine [ZA/ZA]; 4 Drakenstein, 52 Outspan Road, Sunset Acres, 2001 Johannesburg (ZA).</p> <p>(74) Agent: RADEMEYER, Montague, Ampie, John; McCallum Rademeyer & Freimond, P.O. Box 1130, 7 Maclyn House, Bordeaux, 2125 Randburg (ZA).</p> <p>(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,</p> |
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(54) Title: RECOVERY OF COPPER FROM COPPER BEARING SULPHIDE MINERALS BY BIOLEACHING WITH CONTROLLED OXYGEN FEED



(57) Abstract: A method of recovering copper from a copper bearing sulphide mineral which includes the steps of subjecting the slurry to a bioleaching process, supplying a feed gas which contains in excess of 21 % oxygen by volume, to the slurry, and recovering copper from a bioleach residue of the bioleaching process.

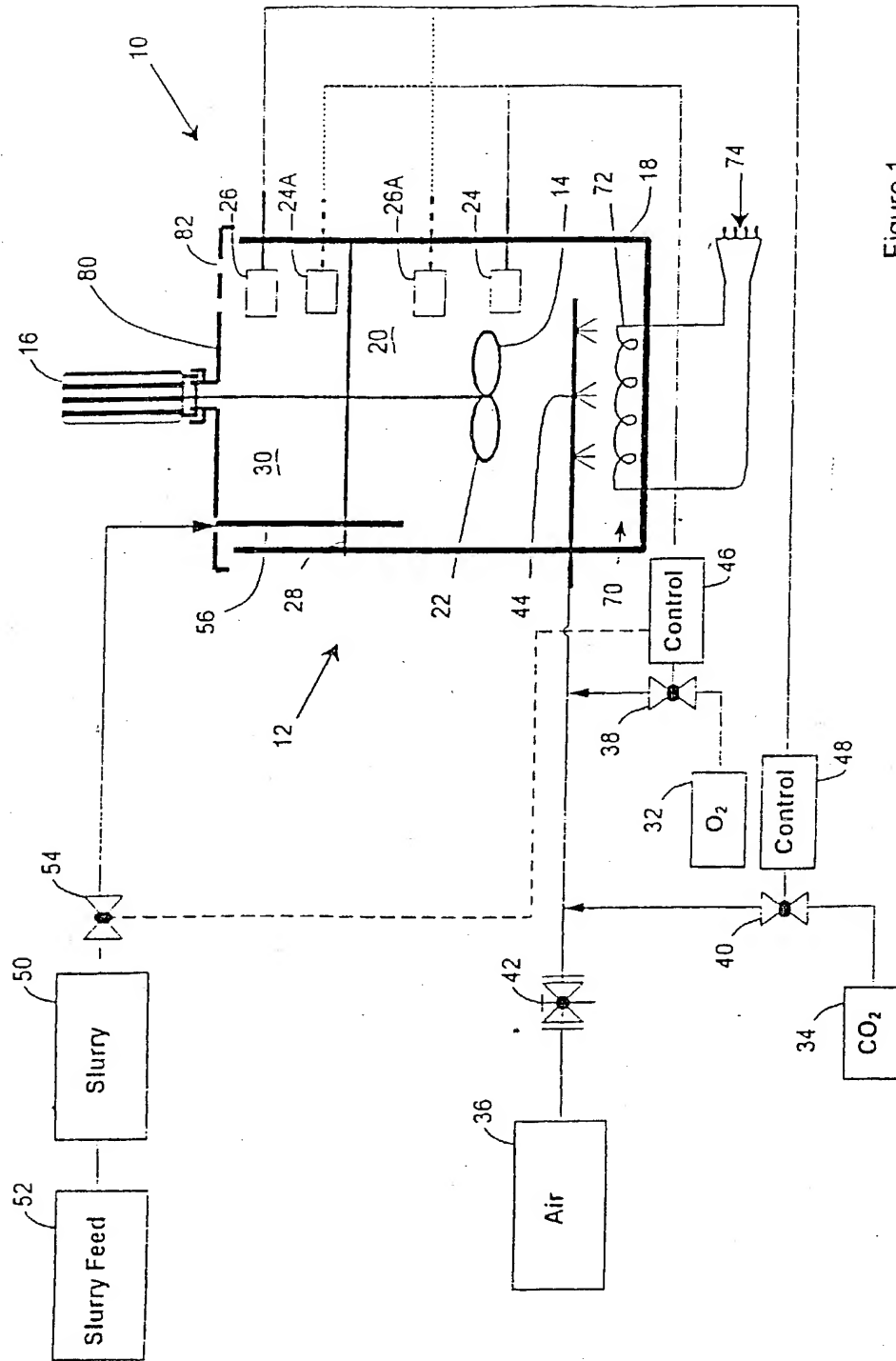


Figure 1

Ferrous Concentration vs. Dissolved Oxygen Concentration

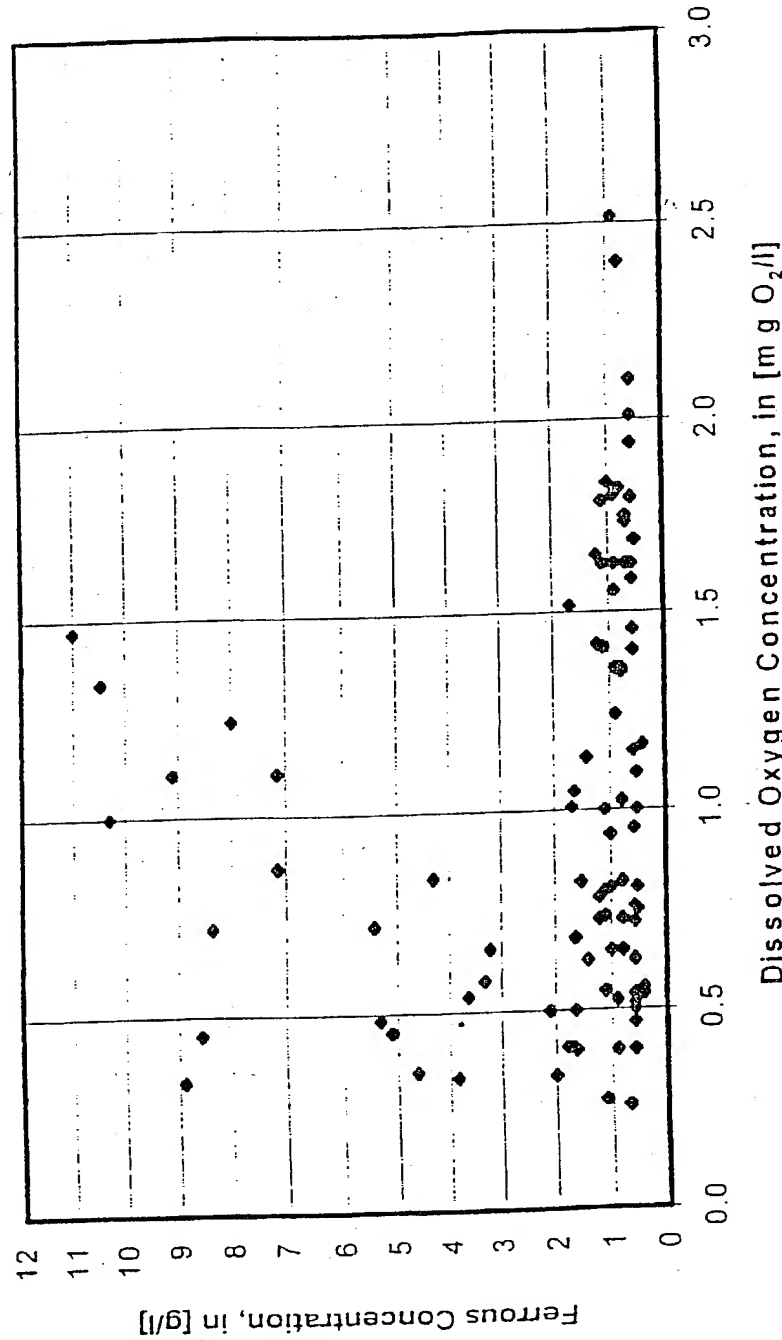


Figure 2 Results Showing The Effect of Reduced Microbial Oxidation On Iron(II) Concentration Levels In Solution As A Result Of Operating At Low Dissolved Oxygen Concentrations

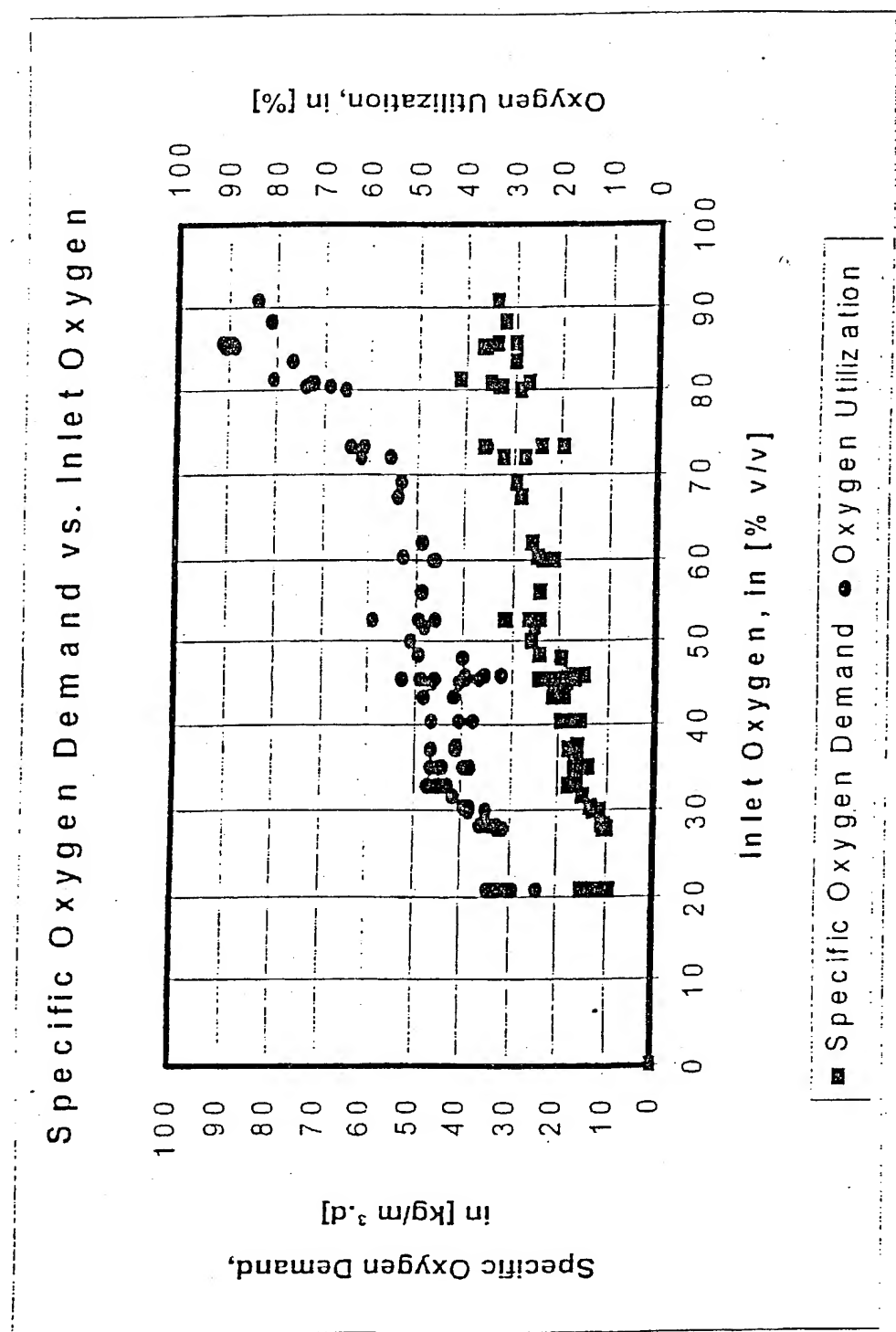


Figure 3 Results Showing The Increase In Specific Oxygen Demand and Oxygen Utilisation Achieved By Increasing The Oxygen Content Of The Inlet Gas Under Controlled Conditions By The Method Of The Invention

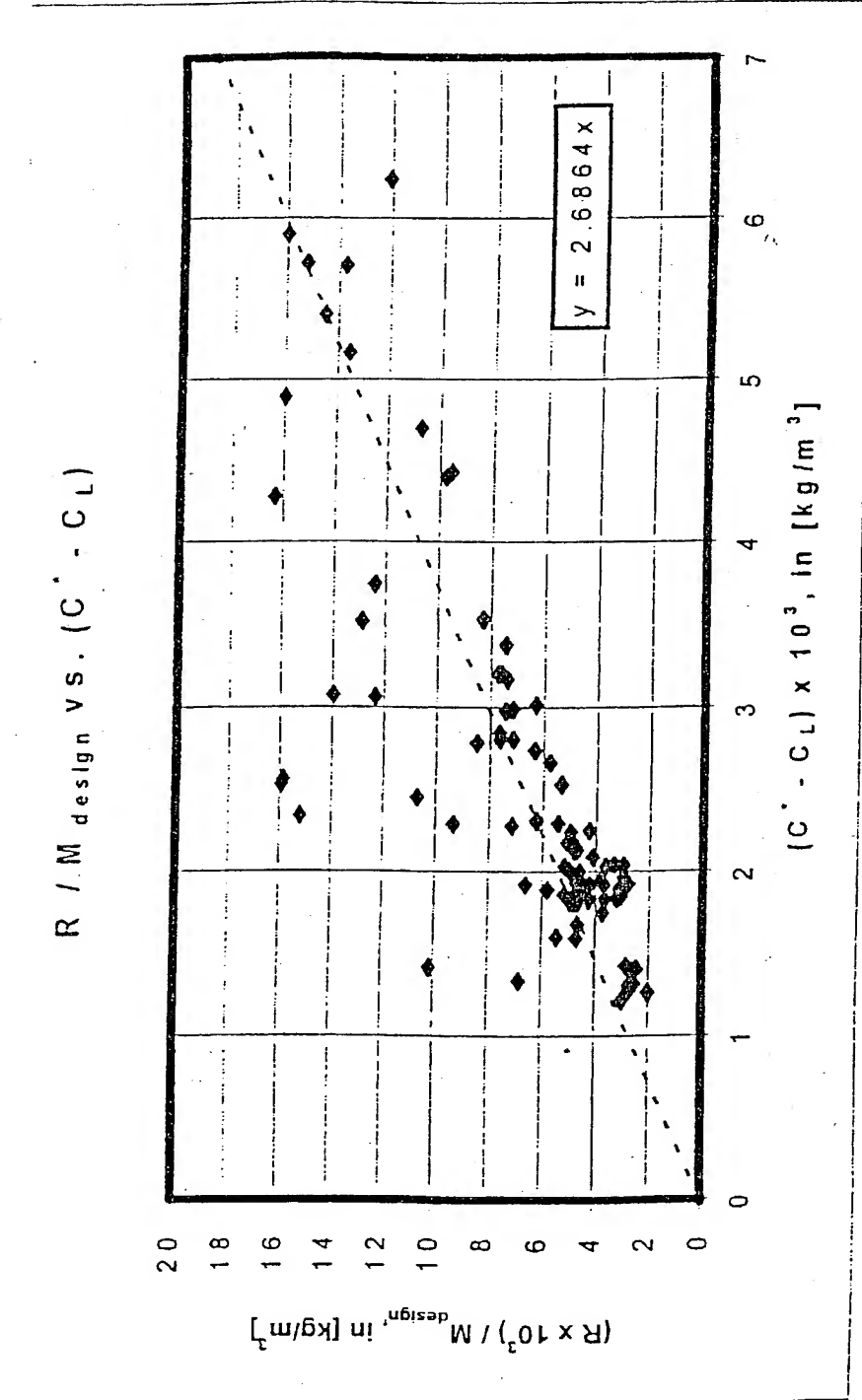


Figure 4 Results Demonstrating The Enhancement Of The Oxygen Mass Transfer Coefficient

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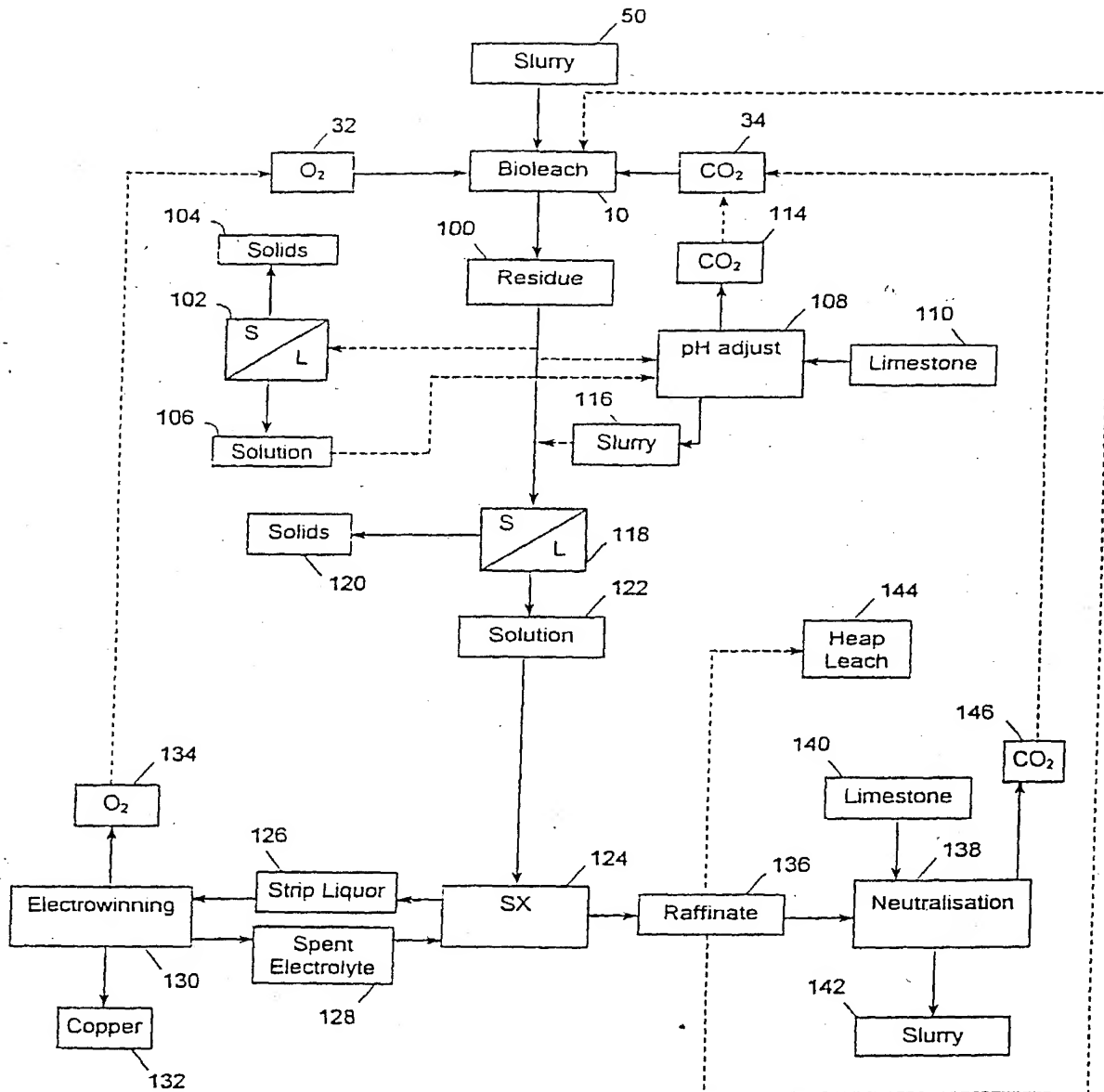


Figure 5

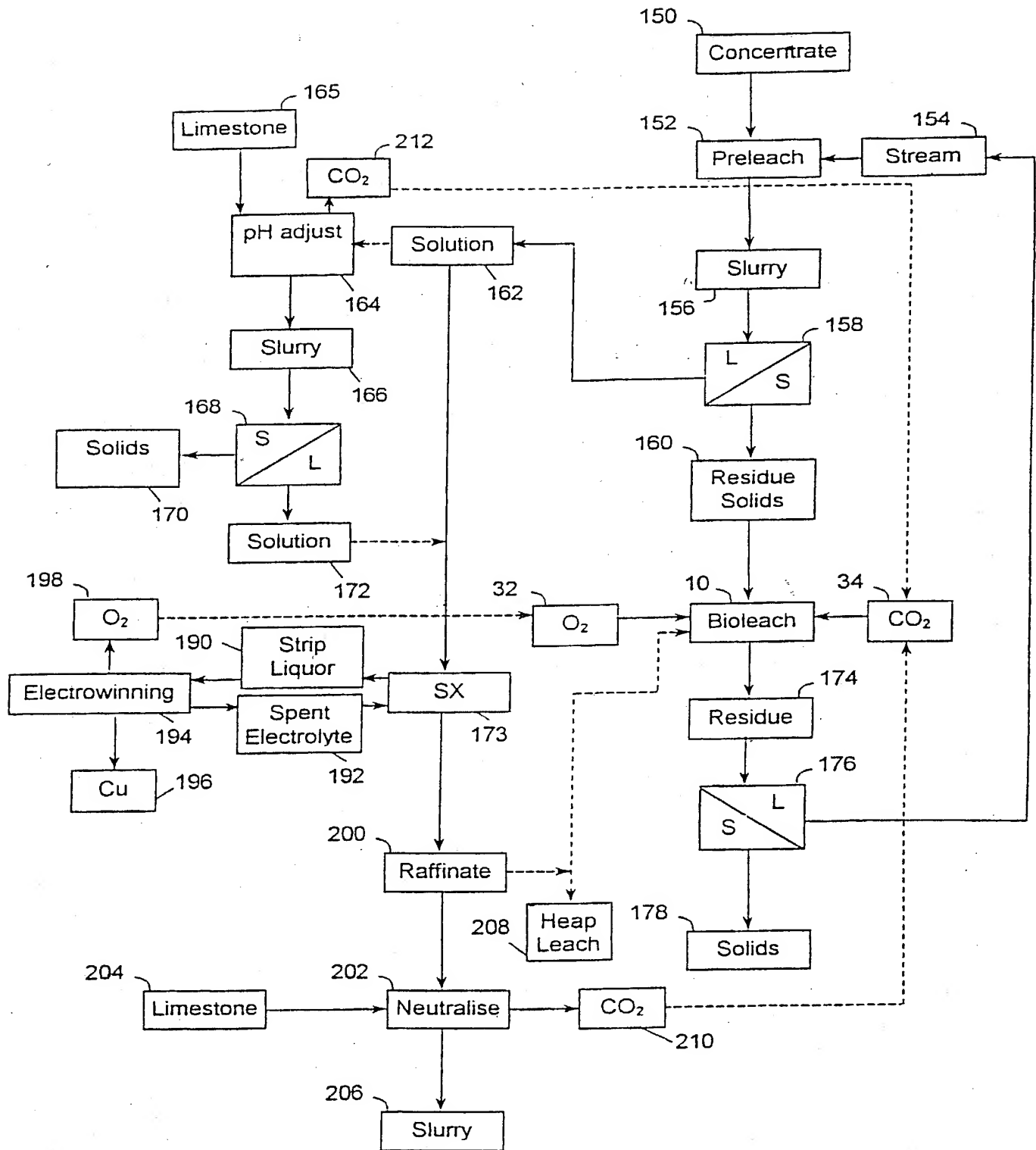


Figure 6

COMBINED DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that:

This declaration is of the following type:

- ☐ original
- ☐ design
- ☐ supplemental
- ☒ national stage of PCT
- ☐ divisional
- ☐ continuation
- ☐ continuation-in-part (CIP)

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed for and for which a patent is sought on the invention entitled:

Recovery of Copper From Copper Bearing Sulphide Minerals by Bioleaching with
Controlled Oxygen Feed.

the specification of which

- ☐ is attached hereto
- ☐ was filed on _____, as
Application No. _____
and was amended on _____
(if applicable)
- ☒ was described and claimed in PCT International Application No. ZA00/00163
filed on 05 September 2000 and as amended under PCT Article 19 on ____ (if any).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any Amendment referred to above.

I acknowledge duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

- ☐ In compliance with this duty there is attached an Information Disclosure Statement. 37 CFR 1.97.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119, of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

- ☐ no such applications have been filed
☒ such applications have been filed as follows.

Prior Foreign Application(s)

<u>99/5746</u>	<u>South Africa</u>	<u>07 September 1999</u>	<input checked="" type="checkbox"/> <input type="checkbox"/>
(Number)	(Country)	(day/month/year filed)	Yes No
 <u> </u>	 <u> </u>	 <u> </u>	 <input type="checkbox"/> <input type="checkbox"/>
(Number)	(Country)	(day/month/year filed)	Yes No

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below:

 (Application Number)

 (Filing Date)

 (Application Number)

 (Filing Date)

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s) listed below, and insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose all information known to be material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

 (Application No.)

 (Filing Date)

 (patented, pending, abandoned)

 (Application No.)

 (Filing Date)

 (patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature _____
(Date)

Residence _____

Citizenship _____

Post Office Address _____